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Fatigue Crack Arrest in a Self-Healing Polymer Composite

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ABSTRACT

A comprehensive experimental program is performed to assess the *in situ* fatigue behavior of a self-healing polymer. A fatigue-life-extension protocol is established for characterizing healing efficiency of the self-healing epoxy under cyclic loading. At moderate ΔK_I and at high ΔK_I, when a rest period is employed, *in situ* healing extends fatigue life though temporary crack arrest and retardation. *In situ* self-healing permanently arrests crack growth at low ΔK_I and at moderate ΔK_I when a rest period is employed. Fatigue crack retardation and arrest result from two primary crack-tip shielding mechanisms: hydrodynamic pressure in the viscous healing agent and artificial crack closure. Application of self-healing functionality to fatigue slows the crack growth rate and increases the fatigue threshold.

1. INTRODUCTION

In addition to failure from monotonic fracture, brittle polymers are highly susceptible to fatigue. Under cyclic loading conditions, cracks grow rapidly and often lead to catastrophic failure. Prevention of fatigue failure currently depends on improvements in accurate life prediction and implementation of economical inspection procedures. The application of self-healing functionality to fatigue crack growth represents a milestone in the development of safer, longer-lasting materials. In this paper, a fatigue-life extension protocol is used to measure the effect of self-healing functionality on fatigue-crack propagation. Depending on fatigue loading and history, self-healing provides significant crack growth retardation or permanently arrest fatigue crack growth.

Application of self-healing functionality to fatigue-crack growth is an innovative approach for preventing fatigue failure of polymer structures. Characterization of fatigue behavior is more complex than monotonic fracture due to the dependence on range of applied stress intensity ΔK_I, frequency f, and ratio of applied stress intensity R. Improvements in fatigue behavior can be achieved in four ways, as illustrated in Fig. 1:

1. Increase the range of stress intensity for crack growth instability ΔK_{ult}.
2. Reduce the crack growth rate da/dN for a given ΔK_I.
3. Reduce the crack growth rate sensitivity to ΔK_I, *i.e.* reduce n.
4. Increase the threshold ΔK_{th} at which crack growth arrests.

We have previously reported on the first and second goals, of increasing the range of stress intensity for crack growth instability and reducing the crack growth rate, through toughening of epoxy with embedded microcapsules [1,2]. In this paper we focus on self-healing [3] and increasing the threshold ΔK_{th} at which crack growth arrests (goal 4). To account for the complexity associated with self-healing under cyclic loading conditions, fatigue-healing efficiency is defined by fatigue-life extension,

$$\lambda = \frac{N_{\text{healed}} - N_{\text{control}}}{N_{\text{control}}}, \tag{1}$$

where N_{healed} is the total number of cycles to failure for the self-healing sample and $N_{control}$ is the total number of cycles to failure for a similar sample without healing.

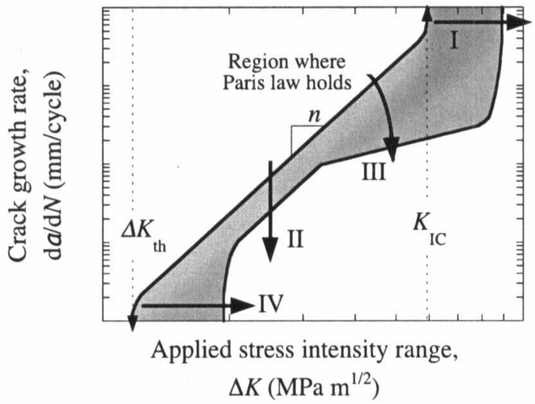

Fig. 1. Representative dependence of fatigue crack growth rate on the applied stress intensity range with the Paris law region.

A limited discussion of healing fatigue damage is present in the literature. Daniel and Kim [4] investigated fatigue damage in asphalt by measuring the decrease in the modulus of elasticity as microcrack growth occurred. After a rest period, gains in stiffness were observed and attributed to healing of the microcracks. Zako and Takano [5] performed a tensile fatigue test on a notched specimen to investigate crack healing in an epoxy composite. The specimen was fatigued until the stiffness decreased by 12.5%. The test was stopped and the crack was healed by application of heat. The fatigue test was resumed with almost full recovery of stiffness. Following healing, the stiffness decreased at a similar rate to the virgin specimen. Both of these investigations considered successful healing as the recovery of stiffness lost due to damage induced by cyclic loading. Neither the effect on crack-growth rate or absolute fatigue life was considered. An extensive literature review and presentation of experimental controls for viscous flow and artificial crack closure is present by Brown [6].

The goal of self-healing in a cyclically loaded material is the extension of component-fatigue-life by retarding crack growth. Optimal self-healing performance will result in complete arrest of fatigue-crack growth following initiation, thus imparting infinite component fatigue-life. To a limited degree, this behavior is observed in many materials when the fatigue load is less than the fatigue threshold ΔK_{th} [7]. In adhesives and composites, where the crack propagation rate is more sensitive to changes in load than for metals and there is considerable scatter in the fatigue crack propagation data, designs are often based on the fatigue threshold rather than on damage tolerance [8]. The fatigue threshold depends on the loading configuration and environmental effects and is a subject of considerable interest in metal fatigue characterization [9]. Investigations of polymer fatigue threshold have focused on composites [8,10] and biomaterials [11].

2. FATIGUE TEST METHOD

The fatigue-crack propagation behavior of the self-healing epoxy was investigated using a constant ΔK tapered double-cantilever beam (TDCB). Further discussion of the fatigue experiment and specimen geometry are provided in Brown et al. [2] and Brown et al. [12] respectively. Side grooves ensured controlled crack growth along the centerline of the brittle specimen. A constant range of Mode-I stress intensity factor ΔK_I was achieved by applying a constant range of load ΔP independent of crack length,

$$\Delta K_I = \alpha \Delta P, \tag{2}$$

which only required knowledge of the geometric term $\alpha = 11.2\mathrm{x}10^3$ m$^{-3/2}$ [12].

Tapered double-cantilever beam specimens were cast from EPON® 828 epoxy resin (DGEBA) and 12 pph Ancamine® DETA (diethylenetriamine) curing agent with 20 wt% 180 μm diameter microcapsules [13] and 2.5 wt% of Grubbs catalyst mixed into the resin. The epoxy mixture was degassed, poured into a closed silicone rubber mold and cured for 24 hours at room temperature, followed by 24 hours at 30° C. Fatigue crack propagation studies were performed using an Instron DynoMight 8841 low-load frame with 250 N load cell. Samples were precracked with a razor blade and pin loaded. Care was taken to ensure the precrack tip was centered in the groove. A triangular frequency of 5 Hz was applied with a load ratio ($R = K_{min}/K_{max}$) of 0.1. Crack lengths were measured optically and by a compliance method [2,6]. The constant ΔK nature of the fatigue test yields a constant crack-growth rate over the majority length of the specimen. Any observed time dependent crack growth retardation or arrest during a given test is therefore an isolated effect of either viscous fluid flow or artificial crack closure.

3. SELF-HEALING OF THE *IN SITU* SYSTEM

In situ healing was investigated by measuring the fatigue-life extension of samples manufactured with 20 wt% microcapsules and 2.5 wt% catalyst. Samples were precracked and immediately cyclically loaded. The crack growth rates associated with fatigue dictate delivery rate of healing agent from rupture of individual microcapsules. The delivery rate must compete with the rate of healing agent evaporation and the rate of the healing reaction. The microcapsule concentration of 20 wt% was chosen to ensure adequate presence of healing agent in the crack plane. Each *in situ* sample was loaded at a prescribed Mode-I stress intensity factor range ΔK_I, frequency $f = 5$ Hz, and load ratio $R = 0.1$. Three different levels of applied range of stress intensity ΔK_I were prescribed: one low-cycle fatigue case and two high-cycle fatigue cases. Low-cycle fatigue refers to the fatigue regime where ΔK_I approaches K_{IC} and rapid crack growth causes sample failure after very few cycles (< 10,000 cycles). For the discussion of self-healing, low-cycle fatigue also refers to the fatigue regime where the time to sample failure is less than the time required for monotonic healing to reach a steady state value. High-cycle fatigue refers to the fatigue regime of low ΔK_I and longer fatigue life (> 10,000 cycles). In the two cases of high-cycle fatigue investigated, the time to sample failure is approximately equal to the time required for self-healing of monotonic fracture or the time to sample failure is longer than the time required for monotonic healing. Each loading condition is investigated with continuous cyclic loading to sample failure and with rest periods to allow for healing with stationary crack faces.

3.1. IN SITU LOW-CYCLE (HIGH K_{MAX}) FATIGUE-HEALING

Under low-cycle-fatigue conditions ($N_{healed} < 10,000$, high ΔK_I), crack propagation in the self-healing epoxy proceeds at a constant rate (Fig. 2a) comparable to a control sample with no self-healing. Control sample data are not shown in Fig. 2a because they are virtually identical to the self-healing sample data. As a result, no healing effects are observed due to rapid crack propagation. Sample fatigue life in the low-cycle-fatigue regime is shorter than the time for the healing agent to gel. The fatigue-life extension is essentially zero, $\lambda \sim 0\%$. Because healing agent gelation has not transpired, the sample halves can be remated, clamped, and allowed to heal. Specimens healed post-failure are capable of supporting a fatigue load, but crack-growth rates at the healed interface are exceedingly fast. Fatigue-healing efficiencies λ for six adhesively-healed *in situ* samples ranged from 0.1–5%.

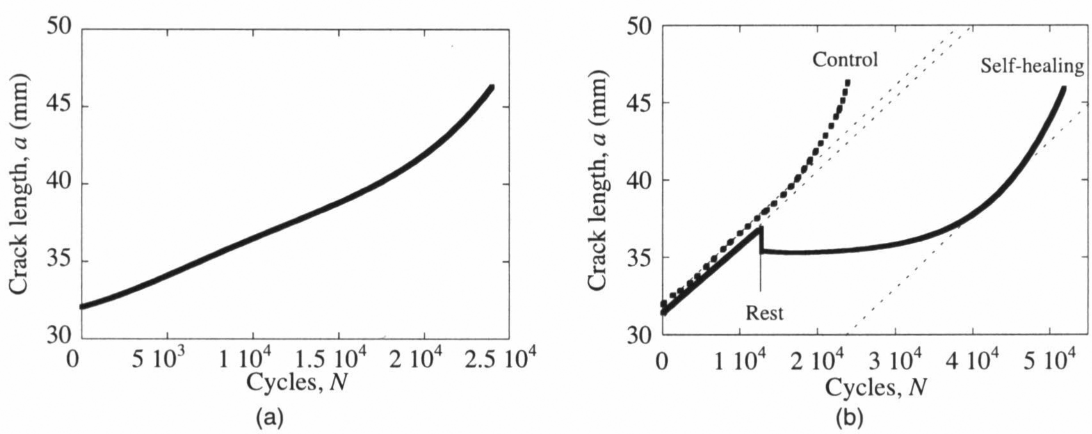

Fig. 2. (a) Crack length *vs.* fatigue cycles of *in situ* sample tested to failure in low-cycle fatigue regime, $\lambda = 0\%$. $\Delta K_I = 0.405$ MPa m$^{1/2}$, $K_{max} = 0.450$ MPa m$^{1/2}$, $K_{min} = 0.045$ MPa m$^{1/2}$, $R = 0.1$, and $f = 5$ Hz. (b) Crack length *vs.* fatigue cycles of *in situ* sample tested in low-cycle fatigue regime with a rest loaded at K_{max}, $\lambda = 118\%$. $\Delta K_I = 0.405$ MPa m$^{1/2}$, $K_{max} = 0.450$ MPa m$^{1/2}$, $K_{min} = 0.045$ MPa m$^{1/2}$, $R = 0.1$, and $f = 5$ Hz.

The effect of rest periods were also investigated; fatigue loading was stopped after a small amount of crack growth and allowed to healing under load at K_{max} for 10 hr. Figure 2b shows the regression and retardation of a fatigue crack achieved by using a rest period at K_{max} to allow self-healing to occur. Similar to the samples repaired by infiltration, healing while loaded at K_{max} is much more effective. Under these conditions, polymerized healing agent forms a wedge at the crack tip, as shown in Fig. 3. The polymer wedge appears as a region of polyDCPD extending ~1 mm from the crack tip in electron micrographs of the fracture plane. The wedge penetrates into the sharp tip of the crack along the majority of the crack front line and has a significant out-of-plane thickness away from the crack tip. Because the interface is formed at K_{max}, it is under zero stress when the applied cyclic load is at K_{max} and under a compressive stress at all other points in the cycle. Under low-cycle-fatigue conditions ($N_{healed} < 10,000$, high ΔK_I) fatigue-life extension λ for *in situ* self-healing epoxy with a rest period at K_{max} ranges from 73–118% for three samples. The 1–2 mm regression of the crack tip due to self-healing calculated from compliance measurements corresponds with direct microscopy measurements of the polymer wedge at the crack tip.

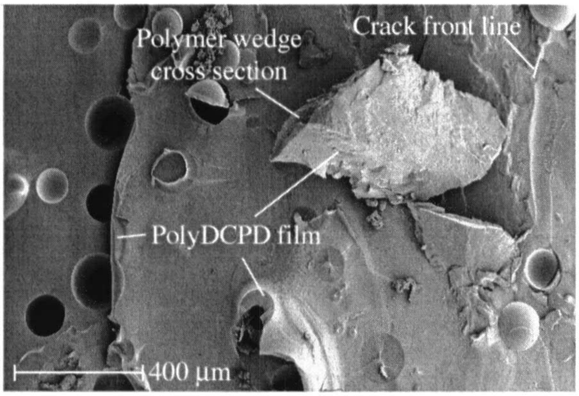

Fig. 3. PolyDCPD wedge at the crack tip of *in situ* sample tested in low-cycle fatigue regime with a rest period under load (see Fig. 2b). Note: The crack propagation is from left to right in all images.

Under high-cycle-fatigue conditions ($N_{healed} > 10{,}000$) the applied range of stress intensity ΔK_I is reduced, decreasing the inherent crack growth rate and increasing the number of cycles to sample failure. In this regime, the sample fatigue life surpasses the time for the healing agent to gel (or quasistatic healing efficiency to develop). Self-healing fatigue-life extension was investigated for a number of samples under this type of loading. The effect of rest periods was also considered. *In situ* samples were precracked and fatigued to failure. A typical plot of crack length *vs.* fatigue cycles is shown in Fig. 4. The large quantity of healing agent released during precracking significantly retards the crack growth, and leads to some crack regression. Following this period of crack arrest the crack eventually grows past the healed precrack (~ 3.5×10^5 cycles). After this point, the fatigue crack growth behavior transitions between periods of constant crack growth rate and periods of crack retardation. During these periods of crack retardation, the crack-tip position corresponds to the location of exposed catalyst. Polymerized healing agent is only present in the vicinity of exposed catalyst and forms an undulating structure with significant out of plane dimension. The concentration and finite dispersion of catalyst leads to localized periods of arrest. Total fatigue-life extension of six samples ranged from 89–213% and is amplified by increasing both the number of arrest events (*i.e.* increasing the number of catalyst particles exposed) and the duration of the individual arrest events.

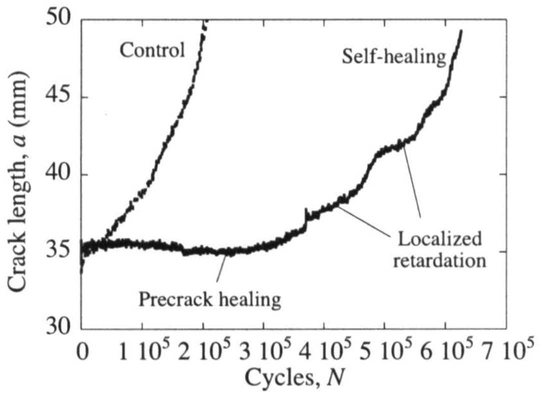

Fig. 4. Crack length against fatigue cycles of *in situ* sample tested to failure in high-cycle fatigue regime, $\lambda = 213\%$. $\Delta K_I = 0.338$ MPa m$^{1/2}$, $K_{max} = 0.376$ MPa m$^{1/2}$, $K_{min} = 0.0.38$ MPa m$^{1/2}$, $R = 0.1$, and $f = 5$ Hz.

The fatigue-life extension due to precrack healing is dramatically improved by adding a rest period at K_{max}. *In situ* samples healed at K_{max} following precracking and tested in the high-cycle-fatigue regime exhibit permanent crack arrest in the two samples tested, shown in Fig. 5a. As in the low-cycle fatigue case healed at K_{max}, a solid polyDCPD wedge forms at the crack tip during the rest period, with similar effect. The retardation elicited by the wedge is more efficient at the lower loading condition. If K_{max} is reduced even further ($\Delta K_I < 0.5\ K_{IC}$), threshold conditions are similarly achieved without a rest period. As shown in Fig. 5b, the precrack regresses and never grows in the time frame of the test. In contrast, the precrack in the control sample is slowly growing at a constant rate. This effect was observed repeatably in four samples tested. Again, the healing agent released during the precrack event forms a partial polymer wedge at the crack tip. Similar to the polyDCPD formed in the cycling crack under higher K_{max}, the wedge formed under lower cyclic load conditions is undulating, however it covers far more of the crack plane.

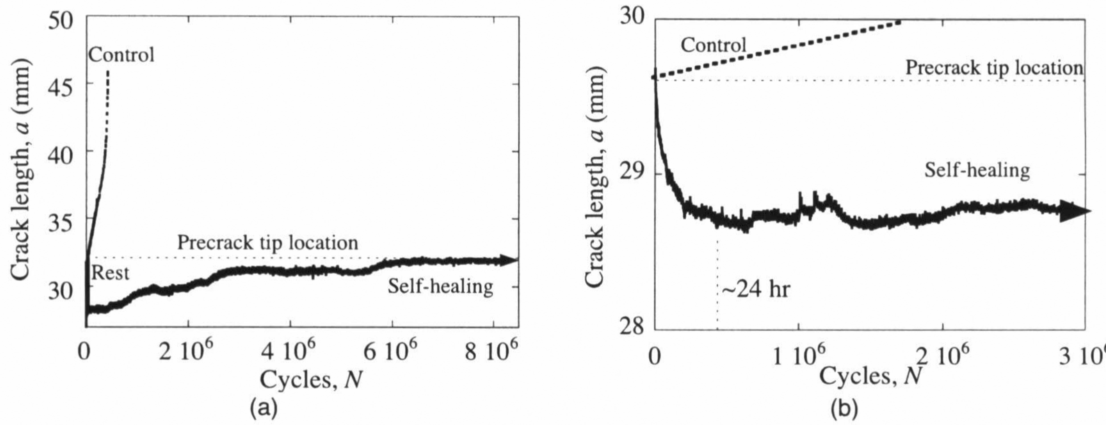

Fig. 5. (a) Crack length against fatigue cycles of *in situ* sample tested in high-cycle fatigue regime with a rest loaded at K_{max}, $\lambda = \infty$. $\Delta K_I = 0.338$ MPa m$^{1/2}$, $K_{max} = 0.376$ MPa m$^{1/2}$, $K_{min} = 0.038$ MPa m$^{1/2}$, $R = 0.1$, and $f = 5$ Hz. (b) Crack length against fatigue cycles of *in situ* sample in the threshold regime, $\lambda = \infty$. $\Delta K_I = 0.270$ MPa m$^{1/2}$, $K_{max} = 0.300$ MPam$^{1/2}$, $K_{min} = 0.030$ MPa m$^{1/2}$, $R = 0.1$, and $f = 5$ Hz.

A summary of life extension values under the different loading conditions is given in Table 1. Significant crack arrest and life extension resulted when the *in situ* healing rate was faster than the crack growth rate. In loading cases where the crack grows too rapidly (maximum applied stress intensity factor is a significant percentage of the Mode-I fracture toughness value), carefully timed rest periods were used to prolong fatigue life. At lower values of applied stress intensity factor, crack growth was arrested completely. The self-healing materials system demonstrates great potential for extending component life under fatigue loading, with the degree of life extension depending on a multitude of operative interaction variables such as stress amplitude, frequency, *in situ* healing rate, and rest periods.

Table 1. Fatigue-life extension from self-healing.

Relative sample failure rate	Range of applied stress intensity, ΔK_I (MPa m$^{1/2}$)	Fatigue-healing efficiency, λ		
		Cycled to failure	Rest period at K_{max}	Healed post failure
$t_{fail} << t_{heal}$	0.7–0.9 K_{IC}	~0%	73–118%	0.1–5%
$t_{fail} \sim t_{heal}$	0.5–0.7 K_{IC}	89–213%	∞*	—
$t_{fail} >> t_{heal}$	<0.5 K_{IC}	∞	—	—

* Infinite fatigue-life extension denotes no optically measurable crack extension after more than 3×10^6 cycles (7 days of testing). Note: $t_{heal} \sim 10$ hr from monotonic fracture.

4. CONCLUSIONS

The crack growth behavior of self-healing epoxy under fatigue loading was investigated. A fatigue-life-extension-based protocol was established for measuring healing efficiency of the self-healing epoxy under cyclic loading. Characterization of this self-healing materials system under fatigue loading presented a significant experimental challenge given the multitude of variables such as stress amplitude, frequency, *in situ* healing rate, and rest periods. Significant crack arrest and life extension resulted when the *in situ* healing rate was faster than the crack growth rate. In loading cases where the crack grew too rapidly (maximum applied stress intensity factor is a significant percentage of the Mode-I fracture toughness value), carefully timed rest periods were used to prolong fatigue life. At lower values of applied stress intensity factor, crack growth was completely arrested, effectively increasing ΔK_{th}. Fatigue-life extension was achieved by a combination of crack-tip shielding mechanisms induced by the self-healing functionality. First, viscous flow of the healing agent in the crack plane retards the crack growth. Second, as the healing agent fully polymerizes a short lived adhesive effect prevents loading of the crack and a long term crack closure effect preventing unloading of the crack tip reduces the crack length and retards additional crack growth.

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